

## **NIRT: Experimental and Computational Investigations of Fluid Properties and Transport Phenomena in Nanodomains with Controlled Surface Properties**

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This research addresses the growing interest in developing manufacturing processes and systems that involve fluids at the nanoscale. There also is continuing evidence that fluid phenomena that occur at the nanoscale are unlike macroscopic behavior. For example, some hydrophobic channels will permit liquid water to exist, while only slightly narrower channels will only permit water vapor to exist. Similar phenomena are expected to manifest when evaluating fluids other than water. The combined experimental, theoretical, and computational investigations focus on the confinement and transport of water, alcohols, amines, and other interesting organic compounds in nanochannels. The generic geometry of the nanofluidic system and fluids considered are representative of important manufacturing systems and processes. The outcomes of the research have significance to nano-rheology, nano-lubrication, control of nanosurface properties, modeling and simulation at the nanoscale, lab-on-a-chip technologies, and other nanofluidic devices. Biosystems and environmental processes that involve nanofluidic transport through membranes and channels will also benefit from the expected outcomes

### **A Molecular Dynamics Study of Water Confined in Hydrophobic Silicalite-1**

Molecular Dynamics simulations were used to understand the behavior of water in silicalite [1]. There are essentially four questions of interest: what is the influence of hydrogen bonding on water diffusion in nanopores and adsorption capacities, what is the physical state of water inside the pores for given thermodynamic conditions, what is the influence of the fluid outside the pores on the fluid inside the pores, and what is the interaction between the pores walls and the water molecules. This last issue could be named the confinement effect.

Molecular Dynamics calculations have thus far been carried out in the simulated pores of

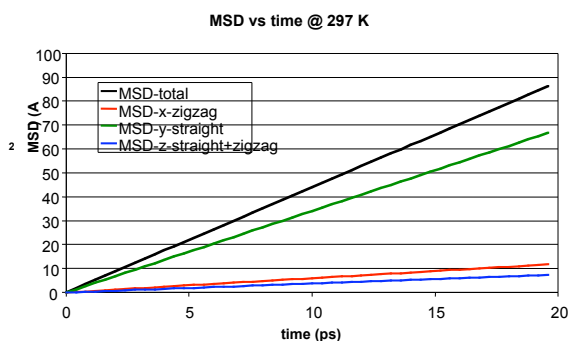


Figure 0 Mean Square Displacement of water molecules in silicalite framework at 297 K as a function of time.

silicalite and zeolite Y, both assumed to be composed of all silica. All the simulations were done in the microcanonical ensemble NVE with constant number of molecules, constant volume, and constant energy. Considering 8 molecules per unit cell the results shown in Figure 1 are typical of those for silicalite-1 at various temperatures

Self-diffusion rates at various temperatures have been determined, as well as radial distribution functions of intermolecular spacing between oxygen atoms, g<sub>OO</sub>, and oxygen and hydrogen atoms, g<sub>OH</sub>. The self-diffusion coefficients

were determined over a temperature range of 250 K – 600 K where normal diffusion occurs. Comparison with experimental data and previous simulations yielded an agreement of the order of magnitude of diffusion coefficients but a discrepancy was observed with experimental data due to some difficulties in synthesizing a pure-silica material and in analyzing the results.

The activation energy for diffusion underlined the complex behavior of water inside silicalite as a single straight line was not observed. Some suggestions were given after considering the hydrogen bonds between water molecules themselves. It appears that at very low temperatures, some clusters are formed. The number of hydrogen bonds decreases very quickly with temperature, and the clusters melt very quickly as a vapor-like phase is formed at room temperature.

Other features of water confined in nanodomains also have been determined:

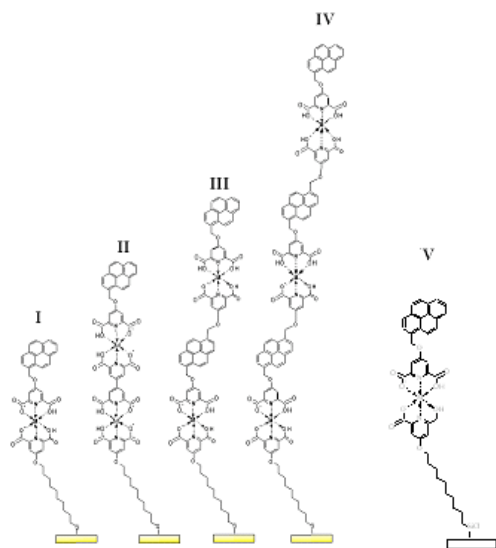
1. For loadings ranging from 1 to 4-5 molecules, the self-diffusion coefficients decrease as loading increases. Then, for loadings ranging from 4-5 molecules to 8-9 molecules per intersection, the self-diffusion coefficients become constant or decrease very slightly.
2. As the number of hydrogen bonds increases with loading, the stabilizing effect becomes more and more important and the self-diffusion coefficient decreases before reaching a limiting value. This limiting value is not surprising because the number of hydrogen bonds per water molecules has a limit too. And since the self-diffusion coefficient depends mainly on the hydrogen bonds, and since the number of hydrogen bonds has a limiting value, the same will be true for the self-diffusion coefficients.
3. Similar calculations have been carried out for water confined in zeolite Y, and those results will be reported elsewhere.

### **Chemical Modification Of Silica And Metal Surfaces With Non-Covalently-Bound Multilayers**

We demonstrate that the surfaces of silica, metals and other materials can be modified chemically with multilayered thin films [2]. These multilayers are constructed by the chemical attachment of alkyl chains to the desired surface through appropriate linking groups to form self-assembled monolayers (SAMs). The alkyl chains (C3-C16) are covalently linked to a pyridine-2,6-dicarboxylic acid group through an ether bridge. A second layer is deposited consisting of transition metal ions such as Cu(II) which bind via non-covalent metal ligand interactions to the nitrogen atom and the carboxylate groups of the pyridine moiety. A third layer containing, in part, another pyridine ligand can be deposited and anchored in place by complexation with the metal ion. Additional layers of metal ions and ligands can be deposited as long as the pyridine binding group is present. This non-covalent method of surface modification provides a rapid and inexpensive way to tailor and thereby control surface wettability.

To date, we have shown that multiple layers can be constructed on both gold and silica as shown in Figure 1. In each case, an aromatic group (pyrene) has been deposited as the final layer. This group was chosen in these prototype systems for two reasons. First it has relatively low wettability (hydrophilicity) and second, it signals its deposition by an unambiguous fluorescence emission. Thus, it acts as a fluorescent probe for deposition. We note that the identity of this

'capping' group can be varied substantially (limited only by synthetic considerations), thereby providing for tunable wettability.



**Figure 2.** Self-assembled multilayers on gold (I-IV) and on quartz (V). Film V on quartz is analogous to Film I on gold.

The sequential deposition of each layer in these films is confirmed by a series of characterization experiments that include cyclic voltammetry (electrochemical conductivity measurements) and impedance spectroscopy in the case of films on metals, plus grazing incidence infrared spectroscopy and contact angle measurements for all films. The latter measurements confirm that substantial changes in wettability occur when the substrate is covered by the SAM (hydrophobic), the metal ions (hydrophilic), subsequent organic ligands (hydrophobic) and subsequent metal ions (hydrophilic), etc. This tunable approach conveniently lends itself to confirming the findings of molecular dynamics calculations as described above since changes in the hydrophilicity of the surfaces of nanodomains can be achieved rapidly.

### Modeling Of Nanoflows With Dissipative Particle Dynamics

A hybrid three-dimensional computational model that combines the molecular and dissipative particle dynamics techniques is under development [3]. This model is applied to unbounded and bounded fluid domains. The DPD model under development uses a Voronoi-lattice to represent dissipative particles (DPs), which now becomes a weighted aggregate of molecular dynamics particles. In this scheme, a DP is no longer defined as a sphere of fixed properties as in classical DPD but rather as Voronoi cells in a gridded periodic domain. The DPD code is applied to a 2-D flow in a nanochannel with the top and bottom boundaries of the simulation domain turned into solid boundaries with proper force-interaction parameters derived from MD.

### References

- [1] For further information email [rwt@WPI.EDU](mailto:rwt@WPI.EDU)
- [2] For further information email [wgm@WPI.EDU](mailto:wgm@WPI.EDU)
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